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Use of Neutron Spectrum Sensitive Monitors for Instrumental Neutron Activation Analysis.

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A fundamental study on the absolute method of neutron activation analysis has been carried out by using three or four monitors which have different sensitivities either to epithermal neutrons or to the thermal neutron temperature. The neutron spectrum index including the neutron temperature can be obtained by a pair of Co-Au or Co-U. The thermal neutron temperature can be estimated by using ^{176}Lu on addition to these. A simple calculation method for obtaining these parameters is presented. Use of antimony as a monitor is discussed.

KEY WORDS : Neutron spectrum / Absolute method / Activation analysis / Neutron temperature /

INTRODUCTION

The instrumental neutron activation analysis can be classified into two categories according to the sort of standards used and consequently to the way of calculation of contents of elements to be determined in samples. One of the methods is the so-called relative method in which samples should be irradiated together with standards consisting of corresponding elements to be determined in samples. Otherwise, elements which gave well defined peaks in the γ-ray spectrum would not be determined in the absence of standards. The way of calculation, howover, is simple by just comparing the total absorption peak areas normalized to cooling periods of both samples and standards.

The other one is sometimes called as the absolute method, the flux monitor method or the comparator method. Depending on the number of comparators used, terms such as single comparator or multi comparator method are commonly used. In principle, the determination method is based on the calculation by using nuclear data such as cross sections and γ-ray abundances and also experimental data such as efficiencies of counting γ-rays and neutron fluxes which are determined by the use of flux monitors of a limited number.

Both methods have merits and demerits. In the former method, it is a troublesome work to make an appropriate combination of standards which cover all the elements detectable in a given sample. On the other hand, the determination can be carried out without any knowledge on nuclear data, neutron flux, neutron spectra and detector efficiencies. The latter method initially developed by Meinke *et al.*[1] makes use of only one flux monitor to determine all the elements in given samples. The method is, however,

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theoretically valid only when the neutron spectra, that is, thermal and epithermal neutron fluxes are known. Uncertainty regarding to nuclear data and the efficiency determination of a detector used will lead to inaccurate results. However, the consistency of the results would be kept as long as the same experimental condition and nuclear data are used. Girardi *et al.*[2] elucidated the method by using cadmium ratio and cobalt as a monitor.

Kim *et al.*[3] measured cadmium ratios to figure out the thermal and epithermal neutron fluxes before or together with the irradiation of samples. Takeuchi *et al.*[4] have developed the method using cobalt or gold as a single comparator. Hoste *et al.*[5] have proposed a combination of flux monitors consisting of elements which are sensitive to thermal and/or epithermal neutrons such as a pair of cobalt and gold and ruthenium isotopes ^{96}Ru, ^{102}Ru and ^{104}Ru. Schmidt *et al.*[6] added iron to ruthenium. The methods of the latter two are theoretically excellent from a view point that neutron spectra and fluxes can be determined in every irradiation without any special device for irradiation facilities.

The present paper describes a simple method for estimating neutron fluxes and spectra including neutron temperature by a set of monitors cobalt, lutetium, gold and/or uranium.

Antimony isotopes, ^{121}Sb and ^{123}Sb were also examined for potential monitors instead of gold and uranium.

EXPERIMENTAL

Flux monitors

Appropriate amounts of standard solutions were pipetted out with a micropipet onto either Millipore Filters (HAWP 45mm dia.) or sheets of aluminum foils of 99.9% purity. After droplets of spotted solutions were air dried, Millipore Filters were sealed in polyethylene bags and packed in sample containers, if necessary. Aluminum foils were used for heavy irradiations and Millipore Filters for low flux irradiations.

Irradiation

Neutron irradiations were performed with pneumatic facilities, the hydraulic system and the E-2 hole installed in KUR. Nominal fluxes of those facilities are listed in Table I. In the hydraulic system, irradiation of any organic materials is not permitted. Therefore, samples were sealed in quartz ampoules instead of polyethylene.

Table I. Nominal Neutron Fluxes in Irradiation Facilities Used in the Present Work.

Irradiation Facility	Neutron Flux (n/cm^2. sec)			Neutron Temp. (°C)
	ϕ_{th}	ϕ_{epi}	ϕ_{fast}	
Hydraulic Tube	8.15×10^{13}	5.95×10^{12}	3.9×10^{13}	100
Pneumatic Tube 1	1.93×10^{13}	6.45×10^{11}	3.2×10^{12}	80
〃 〃 2	2.75×10^{13}	1.09×10^{12}	6.0×10^{12}	80
〃 〃 3	2.75×10^{13}	8.40×10^{11}	4.8×10^{12}	80
E-2 Hole	9.00×10^{10}	6.50×10^{7}	1.30×10^{8}	60

Measurement

Ge(Li) detectors of active volumes of 40cc or 60cc coupled to NAIG 4k channel MCA were to measure γ-ray spectra. Efficiency curves were obtained with IAEA 1μCi, 10μCi standard sources. ^{82}Br, ^{24}Na, ^{75}Se and ^{152}Eu were used as well to interpolate data points.

Data treatment

Programmes named COVIDN and GAMMA both of which were developed by us were used to find peaks, calculate peak areas, identify nuclides and finally give relative weights by normalizing cooling periods, detector efficiencies and nuclear data. COVIDN calculates peak areas in a similar manner to a manual calculation and GAMMA does by fitting peaks to a function of Gaussian plus exponential with the base line of quadratic.

THEORETICAL

According to the Westcott formalism,[7] the effective cross section of a given nuclide can be expressed as follows by assuming that the distribution of the thermal neutron energy is Maxwellian and that of the epithermal is 1/E.

$$\hat{\sigma}=\sigma_0 g+\sqrt{\frac{4T}{\pi T_0}}\,rI' \qquad (1)$$

or

$$=\sigma_0(g+rs) \qquad (2)$$

$$s=\frac{1}{\sigma_0}\sqrt{\frac{4T}{\pi T_0}}\,I' \qquad (3)$$

where

$\hat{\sigma}$: effective cross section.
σ_0: cross section for neutrons with a velocity of 2200 m/sec.
I': resonance integral with a certain cut-off energy in which the 1/v tail is substructed.
r : spectrum index; in well moderated system, r is reduced to the ratio of epithermal to thermal neutron fluxes.
T_0: 293.59°K at which the most probable velocity of Maxwellian neutrons becomes 2200m/sec.
T: neutron temperature with which samples are irradiated.

If we introduce a new spectrum parameter r' as follows, r' includes information on the flux ratio and the neutron temperature and s' becomes a constant which can be calculated from nuclear data. It is obvious that s' equals to zero and g to unity when the cross section of a nuclide obeys the 1/v law.

$$r'=\frac{\phi_{epi}}{\phi_{th}}\sqrt{\frac{4T}{\pi T_0}} \qquad (4)$$

$$s'=\frac{I'}{\sigma_0} \qquad (5)$$

Calculation method of spectrum index from multi flux monitors

If we calculate the weight of an element by measuring the induced radioactivity with using the conventional thermal cross section and a thermal neutron flux, following

expressions conform.

$$W_1'=A_1M_1/C_1n\upsilon_0\sigma_1 \tag{6}$$
$$W_2'=A_2M_2/C_2n\upsilon_0\sigma_2 \tag{7}$$

where

W': weight of an element calculated by using the conventional cross section.
A : measured radioactivity.
M : atomic weight of an element.
C : factor for normalizing radioactivity production and decay, detector efficiency, γ-ray branching ratio isotopic abundance, Avogadro number, etc.
$n\upsilon_0$: thermal neutron flux; an arbitrary number can be used in case only the spectrum index is needed.

The true weight must be expressed by using the effective cross section in a similar manner to the above.

$$W_1=A_1M_1/C_1n\upsilon\hat{\sigma}_1 \tag{8}$$
$$W_2=A_2M_2/C_2n\upsilon\hat{\sigma}_2 \tag{9}$$
$$=\sigma_0(g+r's') \tag{10}$$

The ratio W_i'/W_i becomes the ratio of the thermal cross section to that of the effective. By taking the ratio for two nuclides, a new quatient F can be obtained.

$$F=\frac{W_1'/W_1}{W_2'/W_2}=\frac{g_2+r's_2'}{g_1+r's_1'} \tag{11}$$

If we choose a pair of nuclides g factors of which are close to unity and s' values quite different, the spectrum index r' can easily be obtained.

$$r'=\frac{F-1}{s_1'-Fs_2'} \tag{12}$$

In case a reference neutron field such as a thermal column is available, uncertainty regarding to detector efficiencies and nuclear data can be cancelled out by comparing the results obtained at the same measuring condition.

Let us assume that g factors of monitors are close to unity and the neutron field is purely thermal. F_{th} experimentally obtained can be expressed as the following equation in which each C_i or C_i' is not required to be known.

$$F_{th}=\frac{W_1'/W_1}{W_2'/W_2}=\frac{C_1'C_2}{C_2'C_1} \tag{13}$$
$$F'=F/F_{th} \tag{14}$$

Therefore, we can use arbitrary numbers for C values and the thermal neutron flux. F' thus obtained can be used instead of F in equations for the calculation of r'.

Once r' is obtained, the neutron temperature can be estimated by measuring the ^{177}Lu monitor.

$$W_{Lu}'/W_{Lu}=g_{Lu}+r's' \tag{15}$$

In Table II, g values of several nuclides are shown as a function of temperature together with effective cross sections.

Table II. g Factors and Effective Cross Stctions for Several Nucldes

Nuclide	^{59}Co	In		^{197}Au		^{176}Lu		^{238}U	
Temp. °C	σ	g	σ	g	σ	g	σ	g	σ
20	39.24	1.019	316.0	1.005	150.6	1.701	3631	1.002	4.490
40	39.31	1.023	320.6	1.006	152.4	1.837	3885	1.002	4.608
60	39.37	1.027	325.1	1.008	154.2	1.977	4146	1.002	4.708
80	39.43	1.031	329.6	1.009	155.9	2.118	4409	1.003	4.722
100	39.49	1.035	333.9	1.010	157.6	2.258	4673	1.003	4.833
200	39.77	1.056	355.0	1.015	165.4	2.907	5915	1.005	5.389
300	40.02	1.078	375.2	1.021	172.5	3.418	6912	1.007	5.488
450	40.35	1.113	405.7	1.030	182.1	3.900	7868	1.010	6.490

Effective cross sections are calculated at $r=0.03$ (Westcott's notation) Unit: barn

RESULT AND DISCUSSION

Comparison of cadmium ratio method and the multi flux monitor method.

Comparison of flux ratio ϕ_{epi}/ϕ_{th} determined with the usual cadmium method and with the multi monitor method is presented in Table III. The flux ratio commented as 'nominal' in Talbe III is cited from the published data which were obtained by the cadmium method when the reactor was operated at the stationary power of 1 MW early after the construction. In 1977 when the reactor was operated at the power of 5 MW, flux ratios were measured with both the cadmium and multi monitor methods.

In the multi monitor method, natural uranium, gold and a mixture of chromium and cobalt all of which were in infinite dilution were used as monitors.

The results of both the methods at 5 MW operation agree pretty well each other. On the other hand, more than ten percent deviations were observed between the results of 5 MW and 1 MW operations. Especially noticeable is the difference at the hydraulic system which locates close to the center of the reactor core.

Since the neutron spectrum of an irradiation position in a swimming pool reactor is primarily governed by the structural factors such as the distance from the core or reflectors and secondarily by the environment in irradiation capsules including the quality of the sample itself, it is very likely that the large difference in two independent

Table III. Comparison of Flux Ratios Determined in the Present Work with Those of Nominal

Method	ϕ_{th}/ϕ_{epi} Irradiation Facility				
	pn-1	pn-2	pn-3	hydr.	E-2
R_{Cd}	0.0307	0.0366	0.0341	0.0443	——
M. S.	0.0299	0.0358	0.0332	0.0439	9.53×10^{-4}
Nominal	0.0342	0.0393	0.0365	0.0731	7.27×10^{-4}

R_{Cd}: Determined by measuring cadmium ratio. Cadmium thickness: 0.5mm

M. S.: Multi monitor method

Nominal: Cited from KUR Technical Report KURRI-Tr-80[8]

mesurements in the hydraulic system is attributed to the difference of water contents in the capsules. In the present work, samples covered with a cylindrical cadmium covers were packed with thin aluminum foil and placed directly in the capsule so that the void volume of water in the capsule was kept similar to that on irradiation of practical samples.

Flux ratios of pneumatic facilities thus obtained have been consistent during the period from 1977 up to present except for such extreme cases that polyethylene which

Table IV. Nuclear Data Used in the Present Work

Element	Nuclide	Isotopic Abundance	$T_{1/2}$	E (kev)	Branching Ratio	σ_0	I′
Sc	^{46}Sc	1.00	84.0d	889.2 1120.6	1.00 1.00	26.5	0
Fe	^{59}Fe	0.0031	44.6d	142.4* 192.2 1099.3 1291.6	0.0085 0.028 0.565 0.432	1.13	0.65
Co	^{60}Co	1.00	5.27y	1173.2 1332.5	1.00 1.00	37.0	50
Br	^{82}Br	0.493	35.34h	554.3 776.5 1044.0 1317.4	0.726 0.835 0.271 0.265	26.9	92
Mo	^{99}Mo ^{99m}Tc	0.244	60.0h 6.07h	181.0 739.7 778.2 140.3	0.070 0.120 0.048 0.900	0.130	7.5
Sb	^{122}Sb		2.68d	564.1 692.8 1256.8	0.630 0.327 0.0065	6.25	180
	^{124}Sb		60.3d	602.7* 645.8* 722.8* 1691.0*	0.980 0.071 0.106 0.457	4.32	120
Cs	^{134}Cs	1.00	2.046y	604.6 795.8	0.980 0.880	29.0	450
La	^{140}La	0.9991	40.22h	328.7 487.0 1596.2	0.216 0.465 0.965	8.20	7.5
Yb	^{169}Yb	0.0014	30.7d	177.2 198.0 307.7	0.220 0.35 0.100	3470	23500
Lu	^{177}Lu	0.026	6.71d	113.0* 208.0	0.066 0.111	2100	1478
W	^{187}W	0.386	27.8h	479.5 567.8 685.7	0.260 0.200 0.320	37.8	420
Au	^{198}Au	1.00	2.697d	411.8	0.950	98.8	1505
U	^{238}U	0.99276	2.350d	228.2* 277.6	0.120 0.140	2.74	280

* γ-rays marked were not used because either their branching ratios are inaccurate or they are likely to suffer hindrances by other nuclides.

is one of the best moderator among irradiation samples is packed fully in the irradiation capsule of the size of 25mm inner dia. x 50mm.

Application of neutron spectrum sensitive monitor method to standard samples

Representative elements which have different sensitivities to the flux ratio were examined at various irradiation stations. Nuclear data used are compiled in Table IV and the comparison of amounts taken with those calculated is presented in Table V.

Table V. Determination of Standard Samples by Multiflux Monitor Method.

		Determined values at irradiation positions				
Element	Added (μg)	pn-1 (μg)	pn-2 (μg)	pn-3 (μg)	hydr. (μg)	E-2 (μg)
Au	15.9	15.9	15.6	17.4	15.8	15.5
Br	100	104	109	99	103	—
La	100	97	97	88	92	81
U	11.0	10.7	10.7	10.7	10.8	11.4
Hf	100	98	101	101	94	98
W	100	92	—	94	94	107
Fe	30.0mg	30.7	30.6	30.0	30.2	29.6
Cs	100	90	90	95	90	—
Cr	100	—	96	98	98	—
Yb	100	94	94	92	94	80
Mo	1000	1040	1165	1070	1062	1053
Sc	10.0	11.8	12.6	11.8	11.3	11.9
Lu	100	(213)	(209)	(207)	(226)	(181)
		102 80°C	99.5 80°C	98.6 80°C	102 100°C	91.7 60°C
						97.8 40°C

Although neutron spectra are considerably different, fairly good agreements are obtained. More important is that values determined at different irradiation stations are consistent except for a few cases. In capsules of pneumatic facilities there exist five percent deviation of neutron fluxes. In the E-2 core, the gradient of the neutron flux is considerably high. Therefore, it is difficult at present to obtain reproducible results with that particular irradiation hole.

In case of ^{176}Lu, the discrepancy is quite large. This is because of the g factor which is dependent on the neutron temperature. Data in parenthesis in Table V are not corrected for the neutron temperature. The calculation of g values by Eq. (15) revealed the neutron temperature of pneumatic facilities were 80+5°C which are in good agreement with 'nominal' temperatures. Therefore, determined values of lutetium in Table V were calculated by using 'nominal' temperature. The temperature in the E-2 core was calculated to be 40°C which is again far apart from the 'nominal'. Exact measurements will be possible only when monitors mixed homogeneously are used in the E-2 hole.

Problem on antimony determination

Antimony is a potential element as a spectrum sensitive monitor by the following reasons. The elements consists of two isotopes which are sensitive to both thermal and epithermal neutrons. The isotopic abundances are similar. Halflives of induced radioisotopes by neutron capture reactions are so different that the element can be used as a monitor not only for short-lived nuclides but for the long-lived. By those reasons, efforts have been made to make a large quantity of homogeneous Al-Sb alloy.

In order to check the concentration of the element in the alloy, activation anaysis was performed by both the relative and the absolute methods. The problem arisen was that nuclear data of antimony isotopes are not accurate enough. Some examples of analysis of the alloy by both the methods are compared in Table VI.

As is obvious, concentrations determined with ^{124}Sb by the absolute method are fifteen to twenty percent smaller than those with ^{122}Sb, even though recent nuclear data were used. Whereas, results by the relative method are close to those determined with ^{122}Sb by the sbsolute method. The main reason for these disagreements will be attributed to the inaccurate thermal cross section of ^{123}Sb. The determination of cross sections of antimony isotopes are in progress using the thermal column in KUR. The tentatively recommended value for the thermal cross section of ^{123}Sb is 3.7 barn.

Table VI. Comparison of Concentration of Sb in Al-Sb Alloy Determined by Both the Absolute and Comparative Methods.

	Nuclear Data					Concentration Determined	
	Isotope	σ_0	I′	E (kev)	Branch. Ratio	Absolute (%)	Relative (%)
Old	^{121}Sb	6.25	180	564.1	0.630	0.158	0.161
				692.8	0.327	0.157	0.168
				1256.9	0.0065	0.180	0.175
	^{123}Sb	4.3	120	602.7	0.980	0.134	0.162
				645.8	0.071	0.121	0.152
				722.8	0.106	0.153	0.153
				1691.0	0.457	0.138	0.159
New	^{121}Sb	6.16	180	564.1	0.700	0.152	
				692.8	0.390	0.139	
				1256.9	0.00763	0.171	
	^{123}Sb	4.04	120	602.7	0.983	0.136	
				645.8	0.0723	0.131	
				722.8	0.113	0.149	
				1691.0	0.490	0.140	

Old : Nuclear data which has been used up to present were collected from various data bases such as BNL, Chart of Nuclides published by Kernschungszentrum Karlsruhe in 1974, Atomic Data and Nuclear Data Tables, vol. 13, Nos. 2-3 1974, Academic Press. etc.

New : Cross section and branching ratios were cited from Table of Isotopes, edited by C. M. Lederer and V. S. Shirley, Wiley-Interscience 1978.

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